A Simplified Numerical Study of the Kr/Cl₂ Plasma Chemistry in
Dielectric Barrier Discharge

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Abstract In this paper, the generation of excimers and exciplexe radiation in mixtures of rare
gas with halogen by homogeneous dielectric barrier discharge (DBD) is investigated. The typical
characteristics of an excilamp based on KrCl⁺ exciplexe molecules and the kinetic processes for
the formation and the decay of this molecules in the Kr/Cl₂ mixture are studied. The computer
model developed is based on the Kr/Cl₂ mixture chemistry, the equivalent electric circuit and
the Boltzmann equations. The importance in the kinetic processes of some species such as the
metastable state of Krypton (Kr⁺(3P₀₂,)) and the negative ion of chloride (Cl⁻) is considered.
The results illustrate the time variations of charged species (nₑ, Kr⁺, Cl⁻, Cl⁺, Cl₂⁺, Kr₂⁺), excited
atoms and molecules (Kr⁺(3P₀₂,), Kr⁺(3P₁), Cl⁺, Cl₂), the excimers (Kr₂⁺, KrCl⁺(B), KrCl⁺(C),
Kr₂Cl⁺) and the UV photon concentrations (in 222 nm, 235 nm, 258 nm and 325 nm range). The
effects of chlorine concentration and the total gas pressure in the Kr-Cl₂ discharge on the electric
parameters and radiation emissions are investigated.

Keywords: rare gas, kinetic, homogenous discharge, dielectric barrier discharge, KrCl⁺
excilamp

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1 Introduction

Dielectric barrier discharge (DBD), also called silent
discharge, has found many interesting applications, be-
sides ozone generation. High-power VUV-UV radiation
sources based on DBD discharge are found in many field
of science [1], technology, medicine and for many poten-
tial applications in areas such as microelectronics,
water purification [2] and bacterial surface decontami-
nation [3], medical treatment or photodimerization [4].
The applications of dielectric barrier discharge based on
ultraviolet (UV) or vacuum ultraviolet (VUV) emission
have over the years become an essential technology in
several industrial applications [5].

Compared with the commonly used mercury lamp,
exciplexe and excimer lamps have some advantages in
its simplicity such as high efficiency and low cost [6]. As
an economical and effective configuration, the dielec-
tric barrier discharges of an excilamp have long lifetimes
and no pollutant emission [7]. In DBD, the dielectric
layers have an important role of preventing the arc
passage in the plasma that causes deterioration of the
metal electrodes [8,9]. Recently, attention has focused
on the development of excimers and exciplexe lamps. An
excited dimer or an excimer is a class of molecules that
is formed by the combination of two identical atoms in
the excited state [10]. However, the most common ex-
cimer molecular with a dissociating ground state used
today is based on two different atoms; a rare gas atom is
bound by a halide atom called the exciplex [11]. These
rare gas monohalides can be formed under certain ex-
citation conditions from Ar, Kr, or Xe and F, Br or
Cl. Excilamps are spontaneous radiation sources based
on the transitions of the excimer molecules of rare gas
(RgX₂) [12], halogene gas (X₂), rare gas halide (RgX⁺)
and mercury halide (HgX⁺) to the dissociative and
ground states [13]. This type of excilamp emits incoher-
ent radiation in the ultraviolet (UV: 200~400 nm) and
vacuum ultraviolet (VUV: 100~200 nm) ranges [14].
ELIASSON and KOGELSCHATZ [15] have investi-
gated many different excited species and studied
their wavelength, including rare gas dimmers, e.g: Ar₂⁺(126 nm), Kr₂⁺(146 nm), Xe₂⁺(172 nm) [16~18],
halogen dimer, e.g: F₂⁺(158 nm), Cl₂⁺(259 nm),
Br₂⁺(289 nm), I₂⁺(342 nm) [19] and rare gas halide
exciplex, e.g: ArF⁺(193 nm), ArCl⁺(174 nm),
KrCl⁺(222 nm), XeCl⁺(308 nm) [20~22], as well as a
mercury rare gas excimer (HgNe⁺, HgAr⁺, HgKr⁺,
HgXe⁺) [23]. With the aim of optimizing the discharge
luminance efficiency, some experimental studies have
been conducted on DBD for the KrCl⁺ excilamp [24~27].

Among all known excimers, the Cl₂-based excimers
(Cl₂, XeCl and KrCl) are the most important ones as
they offer short wavelengths and have the most appli-
cation potential, mainly in water purification [28] and
skin treatment for psoriasis or in dentistry. It is known
that UV radiation in the B and C range can efficiently
inactivate bacteria. UV (in all ranges) is also an impor
tant factor in bacterial sterilization using low pressure plasmas [29]. OSNIN et al. investigated the effects of UV radiation on bacteria and mammalian cells [30].

In this work, a computer model including the di-electric and the positive column has been developed to investigate KrCl\(^+\) excilamp behaviour in the case of homogenous discharge. This model describes the electrical and chemical properties of the excilamp. We present in section 2 an overview of the physical and the kinetic models. In section 3, the salient numerical results are presented and discussed. The conclusion of the present work is drawn in section 4.

2 An overview of the physical and the kinetic models:

a. The excimer and exciplex formation and decay in a rare gas halogen mixture:

To understand the formation of excimer KrCl\(^+\) in the discharge, we need to analyze the potential energy diagram (see Fig. 1) and the transition processes from the excited to the fundamental and stable levels of atoms that compose the excited molecule. The excited molecules, also called the excimers, cannot have stable states and thus they must be returned to their dissociative and fundamental ground states and thereby the energy is converted, in the gas medium, to electromagnetic radiation in the UV and VUV ranges. We observe three excited states for the KrCl\(^+\) exciplex molecule, B, C and D, and two fundamental states, A and X. For some molecules the B state has a higher energy than the C state [31]. The B-X and D-A transition have the highest momentum transition and show the strongest fluorescence. The C-A transition is weaker and leads to broad band emission [32]. In the Kr/Cl\(_2\) excilamp the B-X transition in 222 nm is most important compared to the D-A transition in 235 nm and C-A transition in 240 nm. The formation of the excited levels in the KrCl\(^+\) discharge depends on the precursor space density, like the atomic excitation of krypton in the \(\text{KrCl}^*\) transition in 240 nm. The formation of the excited levels compared to the D-A transition in 235 nm and C-A transition in 240 nm.

b. Discharge kinetic processes in the Kr/Cl\(_2\) mixture:

From the energy deposited in the discharge, only a small part is used for the production of excited and ionized atoms or molecules and the majority of the energy is lost in elastic collisions with heavy atoms and molecules. The electrons at the high energy level in the tail of the electron energy distribution function excite or directly ionize rare gas atoms via inelastic collisions:

\[
\text{Kr} + e \rightarrow \text{Kr}^* + e \quad (1)
\]

\[
\text{Kr}^* + e \rightarrow \text{Kr}^+ + 2e \quad (2)
\]

\[
\text{Kr} + e \rightarrow \text{Kr}^+ + 2e \quad (3)
\]

\[
\text{Kr}^+ + 2\text{Kr} \rightarrow \text{Kr}_2\text{Cl}^* + \text{Kr} \quad (4)
\]

\[
\text{Kr}^+ + \text{Cl}^- + \text{Kr}^+ \rightarrow \text{KrCl}^* + \text{Kr}^+ \quad (6)
\]

\[
\text{Kr}_2\text{Cl}^* + 2\text{Kr} \rightarrow 2\text{Kr} + \text{Cl} + h\nu \quad (11)
\]

Fig. 1 Energy diagram for the formation of KrCl\(^+\) from the excited and ionic atoms of chloride and krypton

Ionization via excited states (stepwise ionization) is the most important process in the discharge, which contributes to the formation of rare-gas ions. The rate coefficients of reactions (1), (2) and (3) are calculated as a function of the reduced electric field \(E/N\) by using Bolsig+ software [34] (see Fig. 3).

The production of molecular rare-gas ions via a three-body recombination process is also important:

\[
\text{Cl}_2 + e \rightarrow \text{Cl}^- + \text{Cl} \quad (5)
\]

This dissociative attachment rate is plotted in Fig. 3.

The excimer formation channels are:

\[
\text{Kr}^+ + \text{Cl}^- + \text{Kr}^+ \rightarrow \text{KrCl}^* + \text{Kr}^+ \quad (6)
\]

\[
\text{Kr}_2\text{Cl}^* + 2\text{Kr} \rightarrow 2\text{Kr} + \text{Cl} + h\nu \quad (11)
\]

The first two reactions are called ion-ion recombination and take place in the form of three body reactions with a rate constant of \(1\times10^{-29}T_e^{-4.5} \text{ cm}^6/\text{s} \) [36] and \(1\times10^{-6} \text{ cm}^3/\text{s} \) [37] respectively. The first rate is measured as function of the electronic temperature \(T_e\). The third and the fourth reactions are called harpoonning reactions. The rate coefficient of reaction (8) is estimated to be \(7.3\times10^{-10} \text{ cm}^3/\text{s} \) [38] and for reaction (9) the rate is \(5.5\times10^{-10} \text{ cm}^3/\text{s} \) [39].

At high pressure the triatomic excited molecule Kr\(_2\)Cl\(^+\) is formed, with the rate coefficient at \(1.15\times10^{-30} \text{ cm}^9/\text{s} \) [40], through the three body reaction involving the quenching rare gas atoms with the exciplex:

\[
\text{KrCl}^* + 2\text{Kr} \rightarrow \text{Kr}_2\text{Cl}^* + \text{Kr} \quad (10)
\]

This triatomic excited molecule can give a low intensity of UV emission in 325 nm when it decays:

\[
\text{Kr}_2\text{Cl}^* \rightarrow 2\text{Kr} + \text{Cl} + h\nu \quad (11)
\]
The radiation spectrum of the Kr/Cl₂ gas mixture is essentially determined by the B→X transitions of the KrCl⁺ molecule with a maximum at 222 nm and a rate coefficient of 5.4×10⁹ s⁻¹ [41]. The sum of the transitions C→A (240 nm), D→A (235 nm) and the transitions D'→A' of Cl₂ molecules (258 nm), as well as the transitions of Kr₂Cl⁺ (325 nm) is noted. It is instructive to note that the formation of the desired excimer molecule (KrCl⁺, Cl₂⁺ and Kr₂⁺ in Kr/Cl₂ mixture) occurs at the end of the kinetic chain reaction.

The dielectric barrier discharge configuration in this work uses the planar configuration with two dielectric layers placed between the metallic electrodes. The model of the dielectric barrier discharge developed in this article is based on three main modules: a plasma chemistry module, a circuit module and a Boltzmann equation module. The plasma in the discharge region is investigated by using the homogenous discharge equation module. The plasma in the discharge region is represented by using the homogenous discharge model [42]. The dielectrics and the plasma in the positive column are represented by a capacitance and a resistance, respectively (see Fig. 2).

![Fig. 2](image_url)  
**Fig. 2** Configuration of the electric circuit used and representation of the capacitance equivalent to the dielectrics

The scheme of the dielectric barrier discharge is shown in Fig. 2. The applied voltage $U(t)$ through the discharge is given at instant $t$ by the relation:

$$U(t) = U_d(t) + U_g(t),$$  
(12)

$U_g$ and $U_d$ are the voltages across the gap and the dielectric, respectively.

Here

$$U_d(t) = \frac{1}{C_{\text{dielectric}}} \int I(t) \, dt,$$  
(13)

$C_{\text{dielectric}}$ is the dielectric capacitance.

The electron density in the plasma is a solution of the system’s kinetic equations describing the time evolution of species concentrations involved in the creations or losses of charged particles. It has been shown in Ref. [17] that even with considerable simplification in the description of the high-pressure dielectric-barrier discharges, the electrical and kinetical aspects of the excilamp can still be correctly predicted. The system of equations describing the dielectric and the plasma kinetics are solved as follows: for a given voltage at time $t$, the plasma kinetics equations coupled with the electric circuit equation are solved with the classical GEAR method [43] between instants $t$ and $t + dt$.

### 3 Results and discussions

#### 3.1 Input conditions

For the configuration of the electrodes, the electrical circuit used, and for the Kr/Cl₂ mixture in the dielectric barrier discharge, the excilamp working conditions are: a rectangular applied voltage with amplitude of 6 kV, a pressure of 200 Torr, a gap of 0.9 cm, the electrodes surface of 1 cm², the preionization density of 10⁹ cm⁻³, and the equivalent dielectric capacitance of 1.5 pF (see Fig. 2).

We obtained the collision transport coefficients and electronic frequencies as functions of the reduced electric field $E/N$, by solving the Boltzmann equation in the stationary case and for a uniform electric field. The rates reactions used in the model are plotted in Fig. 3 versus the reduced field for the principal ionization reactions, direct excitation, ionization starting from the metastable state ($^3P_{0,2}$) and resonant state ($^3P_1$) for krypton and the ionization and excitation of chloride.

![Fig. 3](image_url)  
**Fig. 3** Rate coefficients as functions of $E/N$ for Kr (99.8%)–Cl₂ (0.2%) mixture at 200 Torr gas pressure

#### 3.2 Discharge process

##### 3.2.1 Electrical characteristics

The temporal variation of the voltage $U_d$ in the capacitance equivalent to the dielectrics and the voltage across the gap $U_g$ are represented in Fig. 4. The voltage $U_d$ starts to increase until reaching a maximum value which corresponds to the applied voltage, while the discharge voltage $U_g$ decreases after the gas breakdown to reach a low value.

The temporal variation of the current density during the discharge pulse is shown in Fig. 5. When gas breakdown occurs, the current density increases rapidly and reaches a maximum value of 0.086 A at 70.78 ns. The decrease of the current density at the end of the pulse is due to the charging of the dielectric layers by electrons and ions generated in the plasma volume, which reduces the gap voltage and extinguishes the discharge.
3.2.2 Time variation of the charged particles during the discharge pulse

The time variation of the electrons, the krypton, the chloride atomic and molecular ion density are represented in Fig. 6. After the gas breakdown, one can see a fast increase of the charged particles densities in the discharge. Under these conditions the electron density reaches a maximum value of $1.16 \times 10^{11} \text{ cm}^{-3}$, and the dominant ion in plasma is Kr$^+$ (see Fig. 6).

In Fig. 7 the temporal evolution of the excited atom and molecules density are represented. We observe important production of the exciplex KrCl$^*$ (B, C) at the beginning of the pulse with the maximum of $1.2 \times 10^9 \text{ cm}^3/\text{s}$ for KrCl$^*$ (B) and $1.2 \times 10^8 \text{ cm}^3/\text{s}$ for KrCl$^*$ (C) at 60.9 ns. The evolution form of the metastable states ($^3\text{P}_{0,2}$) of krypton governs the evolution of exciplex production. We explain this dependence by the fact that the reaction of the exciplex KrCl$^*$ production is based on the Kr atomic and molecular ion production, which depends on the Kr($^3\text{P}_{0,2}$) concentration.

The photon production by the excimer and exciplex is shown in Fig. 8. We represent the temporal variation of the photon density for 222 nm, 235 nm, 258 nm and 325 nm obtained by the de-excitation of KrCl$^*$ (B), KrCl$^*$ (C), ClCl$^*$ and Kr$_2$Cl$^*$, respectively. The radiative decay at 222 nm is the principal loss mechanism for all states in Kr-Cl$_2$ mixture. The other states of the exciplex, such as KrCl$^*$ (C) and triatomic Kr$_2$Cl$^*$, contribute to the radiation production of the lamp but their intensities are weak. However Cl$^*$ makes an appreciable contribution to UV radiation due to an important concentration of Cl$_2^*$ at the end of pulsation.
3.3 Parametric study in the discharge

The gas pressure and the mixture concentration are two of the major factors that determine the nature of discharge. It is important to note that more uniform and efficient discharge is observed with lower halogen concentration in the gas mixture. In the case of the Kr/Cl₂ mixture, the chlorine concentration did not exceed 1%. Xiao-bo ZHUANG et al. [44] studied experimentally the effect of different parameters on the efficiency of 222 nm emission, as well as the effect of the total pressure and the chlorine concentration in the UV excilamp emission. In our work, the influences of Cl₂ concentration in the gas mixture and the total pressure on the values of the peak current density and the photon densities of KrCl*(B) emission in the 222 nm range are illustrated in the figures below.

3.3.1 Study of the pressure and concentration effect on the current density

Figs. 9 and 10 show that the increase of gas pressure and the chlorine concentration in the mixture leads to a reduction of the maximum current discharge density. In Fig. 9, for the chlorine concentration of 0.2% in the gas mixture and at the pressure of 200 Torr, the maximum of the current density is 89.05 mA. At 250 Torr the maximum is reduced to 23.6 mA and at 300 Torr the maximum is 6.38 mA.

The variation of the chlorine concentration in the discharge mixture has clear influences on the current discharge density. For the total pressure of 300 Torr, the decrease of the Cl₂ concentration includes the diminution of the dissociative attachment process for halogen and the augmentation of the krypton concentration in the discharge gap. Therefore, more electrons are produced by the direct ionization and the ionization of the krypton excited state that contributes to the increase of the current discharge density.

3.3.2 Study of the pressure and concentration effect on the photon densities

In the dielectric barrier discharge, the excimer formation is favored by high collision rates at elevated pressure. Therefore, it is necessary to work at atmospheric pressure in the DBD. In Fig. 11 we observe the diminution of the photon density when the pressure is increased to more than 200 Torr. Therefore, in the KrCl dielectric barrier discharge, the pressure must be limited around 200 Torr for high photon production in the 222 nm range, for an optimally operating lamp.

From Fig. 12 we can see that the decrease of the chlorine concentration in the mixture leads to an increase of the 222 nm photon density production. This is attributed to the increase of the KrCl* exciplex radiation power in the B-X transition.

In agreement with the results of Xiao-bo ZHUANG et al., we observe that for the Kr-Cl₂ mixture, the optimal operating conditions must be a total pressure of the gas at 200 Torr and a chloride concentration between 0.1% and 1.0% of the gas mixture.
4 Conclusion

This work presents an electric and kinetic approach to study homogeneous DBD in a Kr-Cl\textsubscript{2} mixture for the typical operating conditions found in excilamps. With the aim of understanding the kinetic processes, the temporal variations of the gap discharge and dielectric voltages, the discharge current density and the species concentration are calculated. The kinetic study reveals the dependence of UV and VUV production in the metastable state of krypton population. This state makes a great contribution to the production of the KrCl\textsuperscript{*} (B) exciplex, which is responsible for the principal emission in 222 nm, and Cl\textsubscript{2} has an appreciable contribution to UV radiation.

The electric parameters in the dielectric barrier discharge are strongly influenced by the halogen concentration in the gas mixture due to electron loss dominated by electron processes such as dissociative attachment of the halogen gas and ionization of the rare gas. We conclude that for a KrCl\textsuperscript{*} excilamp the optimal operating conditions are at pressure around 200 Torr with low chlorine concentration in the gas mixture.

Finally, we hope that the present paper helps to achieve a good comprehension of the chemical processes in high-pressure Kr-Cl\textsubscript{2} DBD discharge and the optimal operating conditions which can contribute to the optimization of excimer lamp efficiency.

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